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(54) Title: SOLID-STATE GAS SENSORS AND COMPOUNDS THEREFOR (57) Abstract Compounds of the formula $(MWO_4)_x(ZO_2)_{1-x}$, where M is selected from Mg, Mn, Fe, Co, Ni, and Cu and/or Zn, and Z is selected from Sn and Ti, where $0 < x < 1$ are wolframite-based solid solutions which find utility as solid-state gas sensors for sensing carbon-monoxide, ammonia, methane.		

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Solid-State Gas Sensors And Compounds Therefor

This invention relates to wolframite-based solid solution compounds, gas sensors made therefrom, and the detection and measuring of the concentration of various gases with such sensors.

Semiconducting oxide gas sensors have been primarily used for the detection of combustible gases such as carbon monoxide and hydrocarbons. The response mechanism, described in detail elsewhere (eg [1-2]), relies on the bulk resistance of porous solids mainly depending on ionosorbed oxygen species acting as electron traps. Thus, the interaction of a gas with these surface species results in a change in their surface concentration, which consequently affects the solid resistance. Systematic cation substitution in solid-solution materials as a way of understanding the gas response mechanism linked to the surface chemistry has been previously studied for $\text{Cr}_{2-y}\text{Ti}_y\text{O}_{2+x}$ [3,4], $\text{Ba}_6\text{Fe}_x\text{Nb}_{10-x}\text{O}_{30}$ [5], $(\text{CrNbO}_4)_x(\text{Sn}_{1-y}\text{Sb}_y\text{O}_2)_{1-x}$ [6], and $\text{FeNbO}_4\text{-CrNbO}_4\text{-TiO}_2$ [7] and the effects of stoichiometry, microstructure, gas concentration gradients, and surface segregation on gas sensitivity have been observed. Analysis of the variation of conductivity with reactive gas concentration implies that the surface trap state is formally $\text{O}_{\text{ad}}^{2-}$. We have recently shown that this state can be described as an oxygen molecule adsorbed on a surface oxygen vacancy - reduced cation complex [8]. Oxides can be classified according to the sign of resistance change to reducing gases, as 'n' (resistance decrease) or 'p' (resistance increase). A model which rationalises the effects of bulk donor doping has been developed [9] which predicts a switch from n- to p-type response and conductance minimum at some value of the surface acceptor state density dependent on the bulk donor density.

Previous work [3, 8] has considered solid solution series with transition metal ions in high oxidation states. The present work considers solid solution series with transition metal ions in low oxidation states. The divalent transition metal tungstates, AWO_4 ($\text{A} = \text{Mn, Fe, Co, Ni, Cu, and Zn}$), also referred to as NiWO_4 -type tungstates, are members of a large family of structurally related compounds with small cations which crystallize with the wolframite structure [10]. The structure is monoclinic with $Z = 2$ and space group P2/c (C_{2h}^4). For pure FeWO_4 (feberite), $a = 4.730 \text{ \AA}$, $b = 5.703 \text{ \AA}$, $c = 4.952 \text{ \AA}$, and $\beta = 90^\circ 05'$ [11]. The structure consists of a hexagonal close-packed oxygen array in which one-half of the octahedral holes are occupied. The cation

distribution in the octahedral interstices give rise to zigzag chains of skew-edge linked octahedra extending along the c-axis, and in any single chain there is only one type of cation. The zigzag chains are arranged in alternating layers, perpendicular to the a direction. Between layers, the chains are connected by corner-sharing octahedra so that no chain of one type of cation is linked to another of the same cation. The structural similarity between wolframite and rutile implied the possibility of solid solution series of SnO_2 or TiO_2 with the transition metal tungstates, which would allow the systematic investigation of effects of d-electron population on gas sensitivity. Such a study would give a further test of the general model for gas response given earlier and, by comparison of the effects of different gases, might reveal particular effects attributable to some specific chemistry of the surface. The present paper reports this study.

Tungstates have been investigated for other technological applications. Single crystals of zinc tungstate have, in particular, received much attention because of their potential technological significance in applications such as scintillation detectors, photoanodes and masers. Several studies have reported a wide range of properties of these materials. Watterich *et al* [12] have investigated the properties of paramagnetic defects in ZnWO_4 single-crystals induced by electron-irradiation. Intrinsic paramagnetic defects in undoped zinc tungstate crystals have been observed by ESR after electron irradiation. The only hole-type defect was attributed to a hole trapped at an O^{2-} ion near a zinc vacancy. Two electron-excess centers were due to a single electron trapped at an oxygen vacancy where the defects differed in the oxygen vacancy position. Ti(III) centers in reduced ZnWO_4 -Ti single crystals were also examined [13] by ESR methods which resulted in the characterization of a new Ti^{3+} centre expressed as $[\text{Ti}^{3+}\text{-H}]$.

The d.c. electrical conductivity and thermoelectric power of CuWO_4 have been measured [14] in the temperature range 300 to 700 K on single crystals and on polycrystalline pellets. It has been found that CuWO_4 is an n-type semiconductor. The intrinsic nature of the compound is observed above 455 K with an activation energy of 1.06 eV for polycrystalline pellets. Other authors have reported that CuWO_4 can be

considered as an intrinsic semiconductor with a band gap of 1.52 eV [15].

Measurements of a.c. and d.c. electrical conductivity of nickel tungstate indicated [16] that NiWO_4 has a band gap of 2.10 eV. The conduction mechanism above 500 K (with high resistivity $\approx 10^9 \Omega\cdot\text{cm}$ and $E_a = 1.5 \text{ eV}$) was proposed as an electron transfer from one Ni^{2+} to an adjacent Ni^{2+} ion. Such a transfer would lead to the formation of Ni^{3+} ions ($\text{Ni}^{2+} + \text{Ni}^{2+} \rightarrow \text{Ni}^{3+} + \text{Ni}^+$) which would require high energy as both Ni^{3+} and Ni^+ ions are less stable than Ni^{2+} .

Conductivity measurement in CoWO_4 single crystals showed [17] that cobalt tungstate is a p-type semiconductor. The solid exhibited extrinsic behaviour up to 750K ($E_a = 0.64 \text{ eV}$) and intrinsic behaviour above this temperature ($E_a = 1.4 \text{ eV}$) implying a band gap of 2.80 eV.

Single crystals and polycrystalline samples of FeWO_4 were prepared and characterized by Sieber et al. [18]. From high temperature paramagnetic data, the presence of high spin state iron(II) $3d^6$ was confirmed. Qualitative Seebeck measurements indicated p-type conductivity, and the room temperature resistivity of single crystals was $\approx 100 \Omega\cdot\text{cm}$ with an activation energy of 0.16 eV. The p-type conductivity was interpreted as caused by a small amount of iron(III) being present, due to the formation of a small quantity of Fe_2WO_6 , which is able to form a solid solution with FeWO_4 . Another study by Bharati *et al.* [19] suggested that the solid exhibited extrinsic behaviour up to 900K ($E_a = 0.27 \text{ eV}$) characteristic of conductivity governed by impurities or defects, and intrinsic behaviour above this temperature ($E_a = 0.64 \text{ eV}$).

Electrical conductivity of a single crystal of MnWO_4 in the temperature range 300-1200K has been reported [20]. It was found that the dominant charge carriers are holes (p-type material) over the entire temperature range studied. A break in the Arrhenius plot (σ vs $1/T$) occurred around 600K. The activation energy below and above this break temperature was estimated as 0.53 and 0.57 eV respectively.

The A(II)B(VI)O_4 tungstates are potential compounds for use as photoelectrodes for

the photoassisted decomposition of water using sunlight, and as gas detectors because these materials have the possibility of being either p-type or n-type semiconductors. P-type behaviour could be observed when a small amount of one of the transition metals is oxidized, e.g. the introduction of a small amount of iron (III) as Fe_2WO_6 in iron (II) tungstate. In addition, n-type behaviour might be produced when one of the metals in the structure is reduced to a lower oxidation state, e.g. the reduction of W(VI) to W(V). Thus, the ABO_4 tungstates have potential use as either photocathodes or photoanodes in the photoassisted decomposition of water [21,22]. Some metal tungstates and their composites with carbonates have also been investigated for application to semiconductor-type sensors capable of detecting nitrogen oxides at elevated temperature [23].

We have synthesised a range of new wolframite-based oxides and have discovered that they have utility as gas sensitive resistors. They have particular effect for the sensing of carbon monoxide, ammonia, and methane.

The invention is defined by the claims hereinafter.

These new oxides have the formula $(\text{MWO}_4)_x(\text{ZO}_2)_{1-x}$ where M is selected from Mg, Mn, Fe, Co, Ni, Cu, and/or Zn, and Z is selected from Sn and Ti. M can be more than one of Mn, Fe, Co, Ni, Cu, and Zn, and Z can be Sn and Ti in the same compound.

The Wolframites, MWO_4 , can be prepared from aqueous metal nitrate solutions by the addition of ammonium tungstate solution. They are miscible in the solid state with SnO_2 and TiO_2 . The new oxides can therefore be prepared by solid state synthesis from mixed powders of the tungstate with SnO_2 or TiO_2 , generally with calcination at a temperature of 1000-1300°C.

The sintered oxides can be employed as solid state gas sensors, for example as a thick film on an inert substrate and employing high temperature stabilisation, as described in our earlier WO 95/04926. Typically the film is up to 300 microns thick.

Preferred features of the invention will now be described, by way of

example, with reference to the accompanying drawings in which:-

Figure 1 is a graph showing the resistance against time of an $(\text{FeWO}_4)_{0.1}(\text{SnO}_2)_{0.9}$ sensor upon exposure to 1% CO and CH_4 in air at 420 and 510°C;

5 Figure 2 is a graph depicting the resistivity of various oxides of the invention at 400°C with varying TiO_2 and SnO_2 concentration;

Figure 3 shows the conductance activation energy for various oxides of the invention for the temperature range 400-500°C with varying TiO_2 and SnO_2 concentration;

10 Figure 4 shows the sensitivity, as defined below, S_{CO} of oxides of the invention to 1% carbon monoxide in dry air, at 400°C, with varying TiO_2 and SnO_2 concentration;

Figure 5 shows the sensitivity S_{CH_4} of oxides of the invention to 1% methane in dry air, at 400°C, with varying TiO_2 and SnO_2 concentration;

15 Figure 6 shows the sensitivity S_{NH_3} of oxides of the invention to 1% ammonia in dry air, at 400°C, with varying TiO_2 and SnO_2 concentration;

Figure 7 shows the carbon monoxide/methane selectivity in dry air, expressed as $S_{\text{CO}}/S_{\text{CH}_4}$, of oxides of the invention, at 400°C, with varying TiO_2 and SnO_2 concentrations;

20 Figure 8 is similar to Figure 7 but shows the carbon monoxide/ammonia selectivity;

Figure 9 shows the surface cation concentration as a fraction (%) of total surface cation concentration, determined by X-ray photoelectron spectroscopy, for $(\text{FeWO}_4)_x(\text{ZrO}_2)_{1-x}$, with varying TiO_2 and SnO_2 concentrations; and

25 Figure 10 is similar to Figure 9, but for $(\text{CoWO}_4)_x(\text{ZrO}_2)_{1-x}$.

In this specification, gas percentages are by volume.

The wolframites MWO_4 (with M: Mg, Mn, Fe, Co, Ni, Cu and Zn), were prepared by precipitation from aqueous metal nitrate solution by addition of ammonium tungstate solution. The correct preparations were confirmed by X-

ray powder diffractometry using CuK α radiation (Siemens D5000 in transmission, with incident beam monochromator). The electrical resistivity of these preparations were extremely high $R > 10^9 \Omega \cdot \text{cm}$ at elevated temperature $> 500^\circ\text{C}$). The wolframites were miscible in the solid state with SnO_2 and TiO_2 .

5 The complete range of solid solutions $(\text{MWO}_4)_x(\text{Sn-}$

$\text{Ti}[\text{O}_2]_{1-x}$, $0 < x < 1$ and M: Mg, Mn, Fe, Co, Ni, Cu and Zn, was successfully prepared by classical solid state synthesis from mixed powders of the tungstate with SnO_2 or TiO_2 , with a range of calcination temperature $1000 < T < 1300^\circ\text{C}$ and confirmed by X-ray powder diffraction. Overall, a small quantity ($< 5\%$) of impurity phase content Fe_2WO_6 and Cu_2WO_4 were detected in the FeWO_4 - and CuWO_4 -substituted materials.

Gas sensitivity and selectivity measurements were studied on compressed, sintered pellets (13mm diameter, $\approx 2\text{mm}$ thick) as previously described [3-7]. The electrical resistance of the pellets was first stabilized in dry air at 400°C for 2h. Carbon monoxide, ammonia and methane at low concentration in air were introduced into the rig and the pellet resistance measured at 400 and 500°C . Fig 1 illustrates the typical experimental routine used, and results obtained. Gas sensitivity, S , was calculated as $S = \Delta\sigma/\sigma_o = (R_o - R)/R$, where σ denotes conductivity and R resistance (σ_o , R_o in pure dry air). Hence, a resistance decreasing response is recorded as a positive value and a resistance increasing response as a negative one.

X-ray photoelectron spectroscopy (XPS) was performed (VG ESCALAB 220i XL) using focused ($300\text{ }\mu\text{m}$ spot size) monochromatised Al-K α radiation. The scans were acquired with a step size of 100 meV and the spectrometer pass energy was 20 meV. The binding energies were referenced to the hydrocarbon C 1s peak at 284.80 eV and the sample charging was controlled with a 3 eV flood gun.

The compounds studied covered the range from d^5 to d^{10} with TiO_2 (d^0) and SnO_2 (d^{10}) as end members. Fig 2. shows electrical resistivity as a function of composition at 400°C .

Even small substitutions of Ti or Sn ($x = 0.1$) brought the resistivity into a measurable

range ($5 \cdot 10^4 \leq \rho (\Omega \cdot \text{cm}) \leq 2 \cdot 10^6$). It is notable that small substitutions of FeWO_4 into either TiO_2 or SnO_2 greatly decreased the resistivity. The behaviour is in contrast to the effect of a direct substitution of Fe, which causes a marked resistivity increase. For small substitutions of NiWO_4 into TiO_2 and SnO_2 , the resistivity increased by a factor of two and remained high upon further substitution. Substitutions of the other tungstates gave resistivities clustering in a fairly narrow band well separated from either of these two extremes.

A rough estimate of the activation energies for conduction E_A , was calculated from the resistivities of the materials at 400 and 500°C (Fig 3). Overall, the activation energies were higher for SnO_2 -substituted materials than TiO_2 , which is consistent considering the band gaps of pure TiO_2 and SnO_2 to be respectively, 3.0 eV and 3.6 eV. The NiWO_4 - and FeWO_4 -substituted materials respectively exhibited the highest and lowest activation energy values, which tends to agree with the literature results given in the Introduction. All activation energies for the rest of the substituted materials were clustered between these values. There was an obvious and quite general pattern of variation of E_A with composition for all the compounds: a marked change in activation energy with small substitutions at either end of the series, and a monotonic but relatively small variation with composition between these limits.

Table 1. shows the of resistance changes of $(\text{MWO}_4)_x(\text{M}'\text{O}_2)_{1-x}$ ($\text{M} = \text{Mn, Fe, Co, Ni, Cu, Zn}$, and $\text{M}' = \text{Sn, Ti}$) upon exposure to wet air, 1% CO , 0.1% NH_3 , and 1% CH_4 in air sign ('+' means resistance increase on change of gas from dry to wet air or from dry air to dry air containing the test gas). Table 1 also shows the magnitude of the sensitivity to water vapour, calculated as $|S_{\text{H}_2\text{O}}| = |(R_{\text{dry}} - R_{\text{wet}})/R_{\text{wet}}|$, where R_{wet} denotes the resistance in air saturated with water vapour at room temperature ($\approx 20^\circ\text{C}$). The reactive gases CO , CH_4 and NH_3 were consistent in their classification of the materials as n- or p-type (figs 4-6, wherein $S_{\text{gas}} = (R_0 - R_{\text{gas}})/R_{\text{gas}}$ meaning that a resistance decrease gives a positive sign for S). However, the sign of response to water vapour was not always consistent. The effect of even small substitutions of the tungstates were greatly to decrease the sensitivity of SnO_2 to water vapour, $|S_{\text{H}_2\text{O}}|$ shifting typically from 1.4 to less than 0.2 for all the tungstates substituted materials. The

magnitude of the response to water vapour varied systematically along the transition series: $Mn < Fe, Co < Ni, Cu < Zn$. The cases where the sign of the electrical response to water is different to that of the other gases demonstrate that the mechanism of response to water may be different to that of the other gases.

Table 1. Sign of resistance changes of $(MWO_4)_x(M'O_2)_{1-x}$ ($M = Mn, Fe, Co, Ni, Cu, Zn$, and $M' = Sn, Ti$) upon exposure to wet air, 1% CO, 0.1% NH_3 , and 1% CH_4 in air ('+' means resistance increase on change of gas from dry to wet air or from dry air to dry air containing the test gas). and sensitivity to water vapour $|S_{H_2O}| = |(R_{dry} - R_{wet})/R_{wet}|$ (dry \rightarrow 100% RH at 20°C).

		TiO ₂		←		X _{wolframite}		→		SnO ₂	
		0.1	0.3	0.7	0.9	1	0.9	0.7	0.5	0.3	0.1
Mn	gas	-	+	+	+		+	+	-	-	-
	H ₂ O $ S_{H_2O} = 0.04 \pm 0.03$	-	-	-	-		-	-	-	-	-
Fe	gas	-	-	-	+		+	-	-	-	-
	H ₂ O $ S_{H_2O} = 0.1 \pm 0.07$	-	-	+	+		+	+	+	+	-
Co	gas	-	-	+	+		+	+	+	-	-
	H ₂ O $ S_{H_2O} = 0.11 \pm 0.06$	-	-	+	+		+	+	+	-	-
Ni	gas	-	-	-	-		-	-	-	-	-
	H ₂ O $ S_{H_2O} = 0.2 \pm 0.1$	-	-	+	+		+	+	+	-	-
Cu	gas	-	-	-	-		-	-	-	-	-
	H ₂ O $ S_{H_2O} = 0.2 \pm 0.1$	-	-	-	-		-	-	-	-	-
Zn	gas	-	+	+	+		+	-	-	-	-
	H ₂ O $ S_{H_2O} = 0.44 \pm 0.2$	-	+	+	+		+	+	-	-	-
TiO ₂						SnO ₂					
gas		-				-					
H ₂ O S_{H_2O}		0.2				1.4					

Several points are worth noting concerning the effect of composition on sensitivity. As expected, a notable feature is that, with change in composition along both series, the behaviour for some materials changes from 'n-type' (resistance decrease in the presence of the reducing gas) to 'p-type' (gas causes a resistance increase). Only the Ni- and Cu-based materials remained n-type along both series (SnO_2 and TiO_2). These two sets of materials did show a minimum in sensitivity across the range. For the Ni series, the minimum was on the TiO_2 side, whereas for the Cu series it was on the SnO_2 side. The n-type compounds exhibited much higher sensitivity to CO than the p-type materials but for CH_4 , the differences between n- and p-type materials were not so marked. The Co series was notable in showing a rather strong p-type sensitivity to CH_4 on the SnO_2 branch, just before the n-p transition. The n-p transition was found over the same composition range for all the reactive gases. Considering the mole fraction of tungstate, y , at which the n-p transition takes place, the sequence along the TiO_2 branch is $\text{Zn} < \text{Mn}$, $\text{Co} < \text{Fe}$ and along the SnO_2 branch is $\text{Co} < \text{Mn} < \text{Zn}$, Fe , so the zinc compound was notable in showing asymmetrical behaviour with respect to the two end members. There was a remarkable maximum in the sensitivity to CO at $y = 0.3 - 0.5$ along the SnO_2 branch, for the Fe, Ni, Cu and Zn series, but not for the Mn or Co series. Any such maximum along the TiO_2 branch was not nearly so marked. For sensitivity to methane, a similar maximum was observed, but only for the Ni series. The Ni series on the SnO_2 side was interesting because small substitutions produced a decrease in sensitivity to both CO and CH_4 then further substitution caused a marked increase in sensitivity (n-type) to the maximum.

The carbon monoxide-methane selectivity of all the compounds determined at 400°C is given in Fig 7, and the carbon monoxide-ammonia selectivity with the Mn, Fe and Zn compounds in Fig 8. The Mn, Co, Ni and Cu compounds showed a very stable CO/CH_4 selectivity along both branches (Fig 7) varying from 1 for Mn to 5 for Cu. For Fe and Zn the selectivity remained stable along the TiO_2 branch, but then went through a strong maximum along the SnO_2 branch, increasing by a factor up to 10. The Mn and Fe compounds showed a stable CO/NH_3 selectivity ($0 < S_{\text{CO}} / S_{\text{NH}_3} < 1$) along both series. The Zn compounds however exhibited a different behavior with a high selectivity (up to 7) along the TiO_2 branch (Fig 8).

Fig. 9 and 10 give the surface concentration (atom%) vs. TiO_2 and SnO_2 mole ratio obtained by XPS surface analysis for the Fe- and Co-based materials. It is quite clear from these diagrams that the switch from n-type to p-type gas sensitivity appeared to occur when the surface concentration of Ti and Sn started to decrease significantly. For both series there was a clear segregation of W to the surface corresponding to the suppression of the other cation, particularly the transition metal cation. This segregation was not found for the pure MWO_4 . Titanium seemed to be present at the surface more or less in the concentration expected from the bulk composition. In the n-type range, Sn was repelled from the surface in the Fe-series; the effect was not so marked in the Co-series.

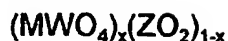
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CLAIMS:-

1. A compound of the formula:



where M is selected from Mg, Mn, Fe, Co, Ni, Cu, and/or Zn, and Z is selected from Sn and Ti, where $0 < x < 1$.

2. A compound according to claim 1 when in the form of a wolframite-based solid solution.

3. A compound according to claim 1 or 2 wherein M is a single one of Mg, Mn, Fe, Co, Ni, Cu or Zn.

4. A compound according to any preceding claim wherein Z is a single one of Sn or Ti.

5. A gas sensor having at least one pair of electrodes in contact with a compound as claimed in any of claims 1 to 3.

6. A gas sensor according to claim 5 wherein the compound is disposed as a film on an inert substrate.

7. A gas sensor according to claim 5 or 6 wherein the film is up to 300 microns thick.

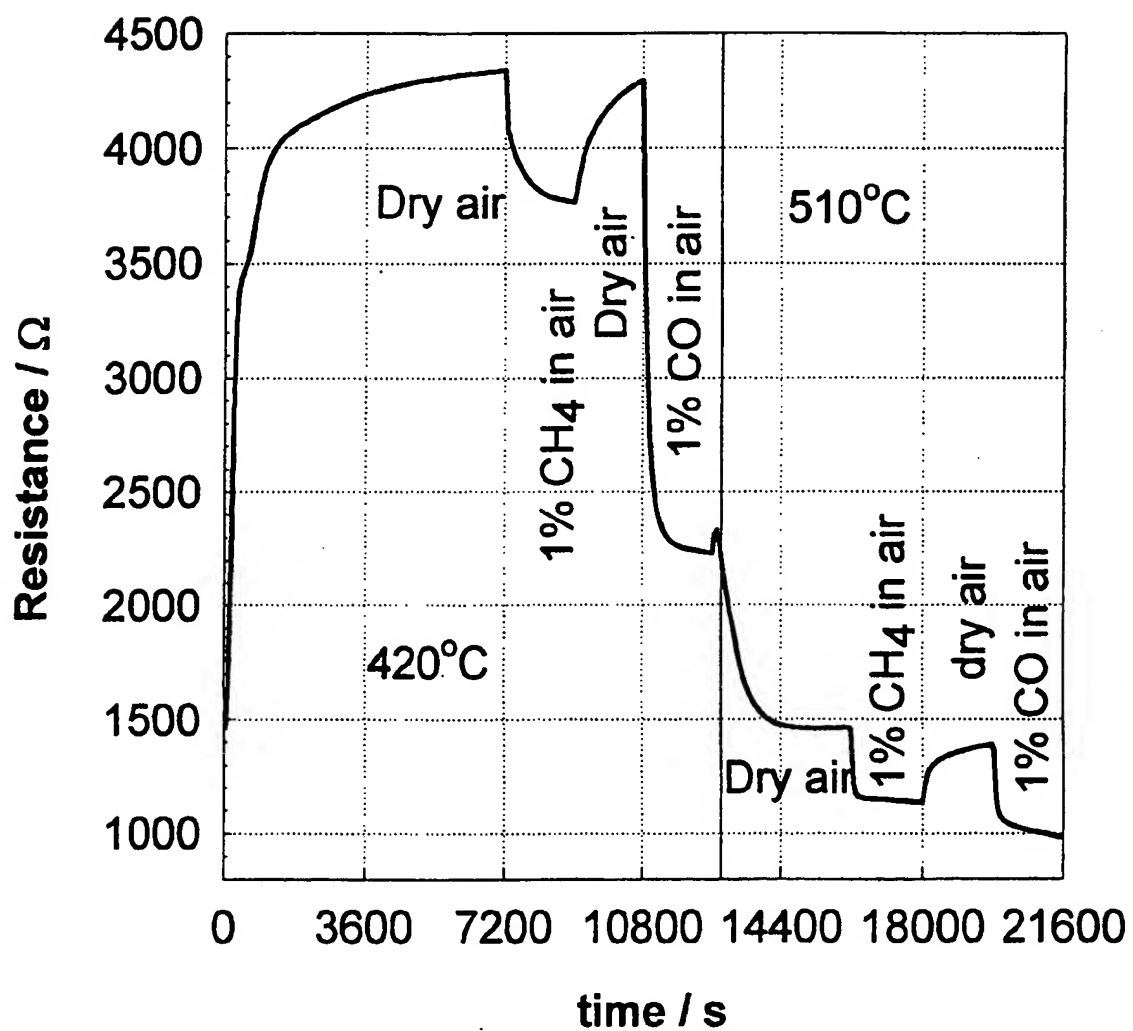
8. Use of a gas sensor according to any of claims 5 to 7 for detecting, or measuring the concentration of a gas in a gas mixture.

9. Use of a gas sensor according to claim 8 wherein the gas is carbon monoxide, methane or ammonia.

10. Use of a gas sensor according to claim 8 wherein the gas mixture contains air.

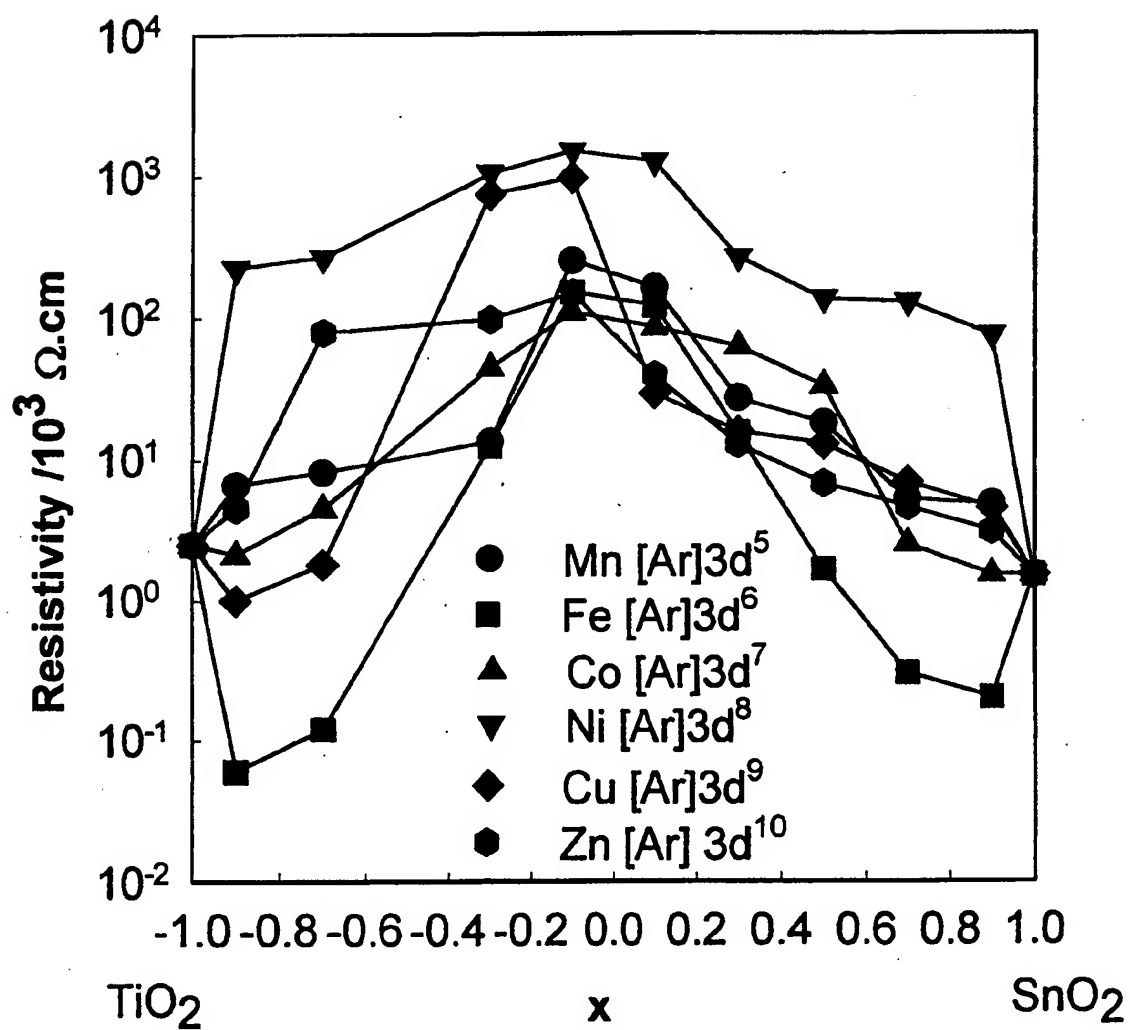
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FIG. 1



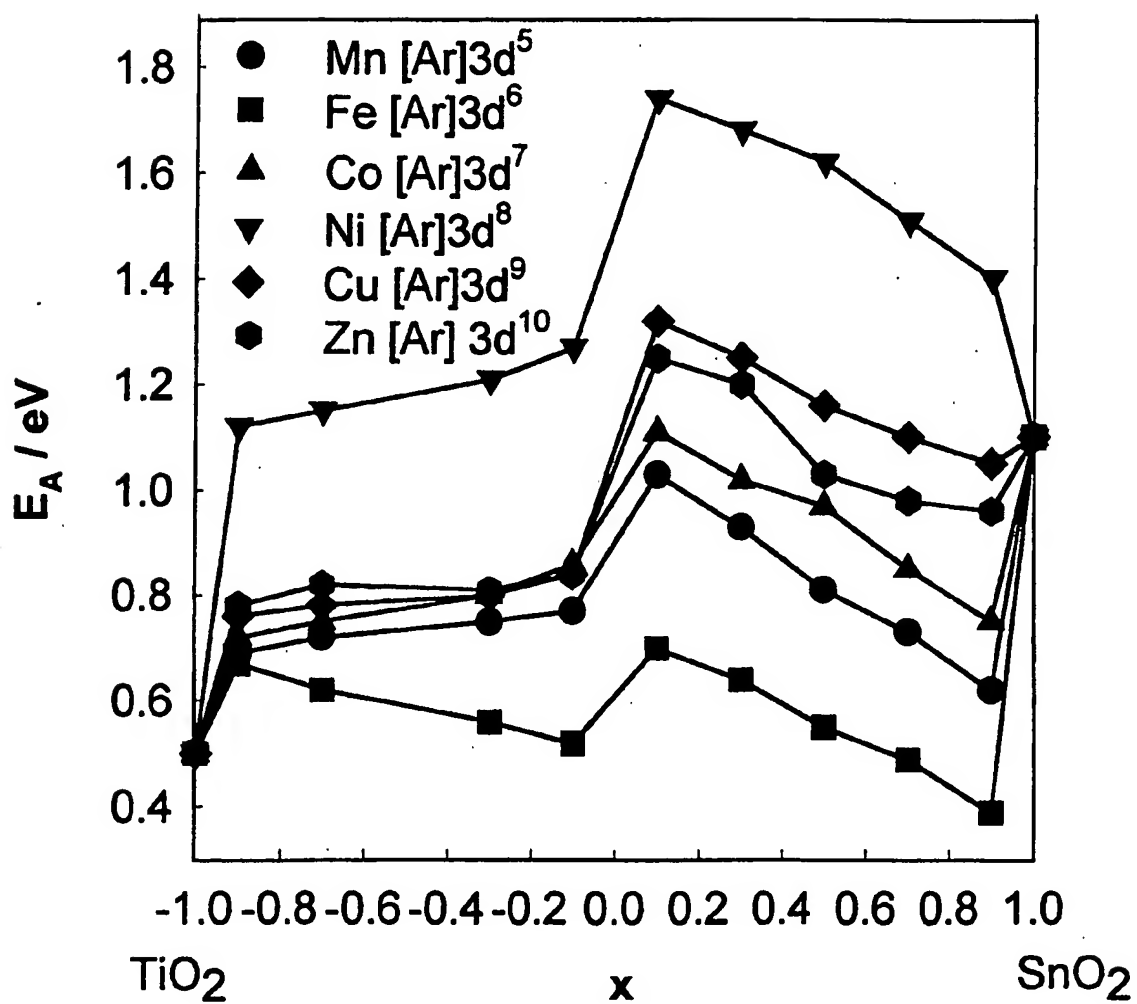
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FIG. 2



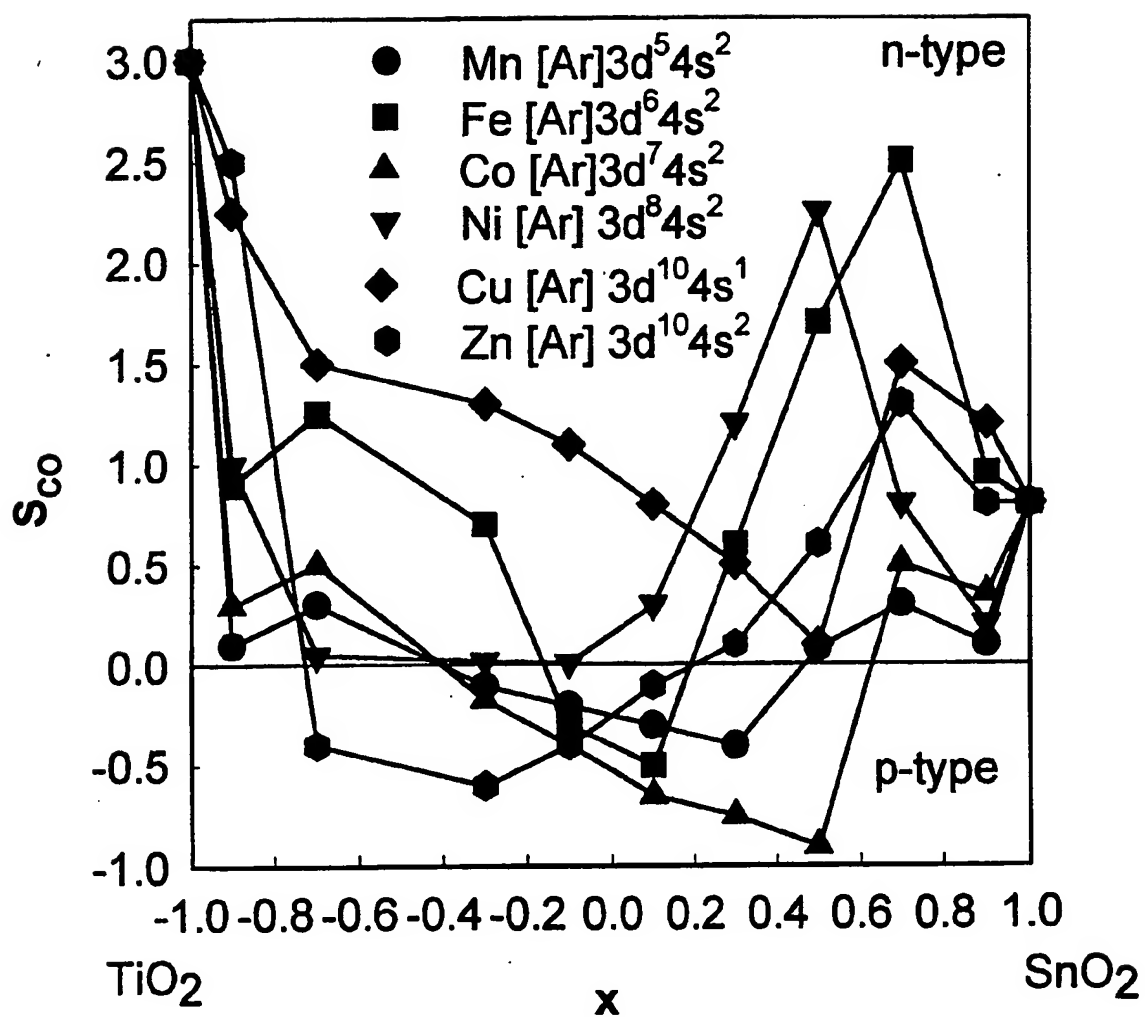
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FIG. 3



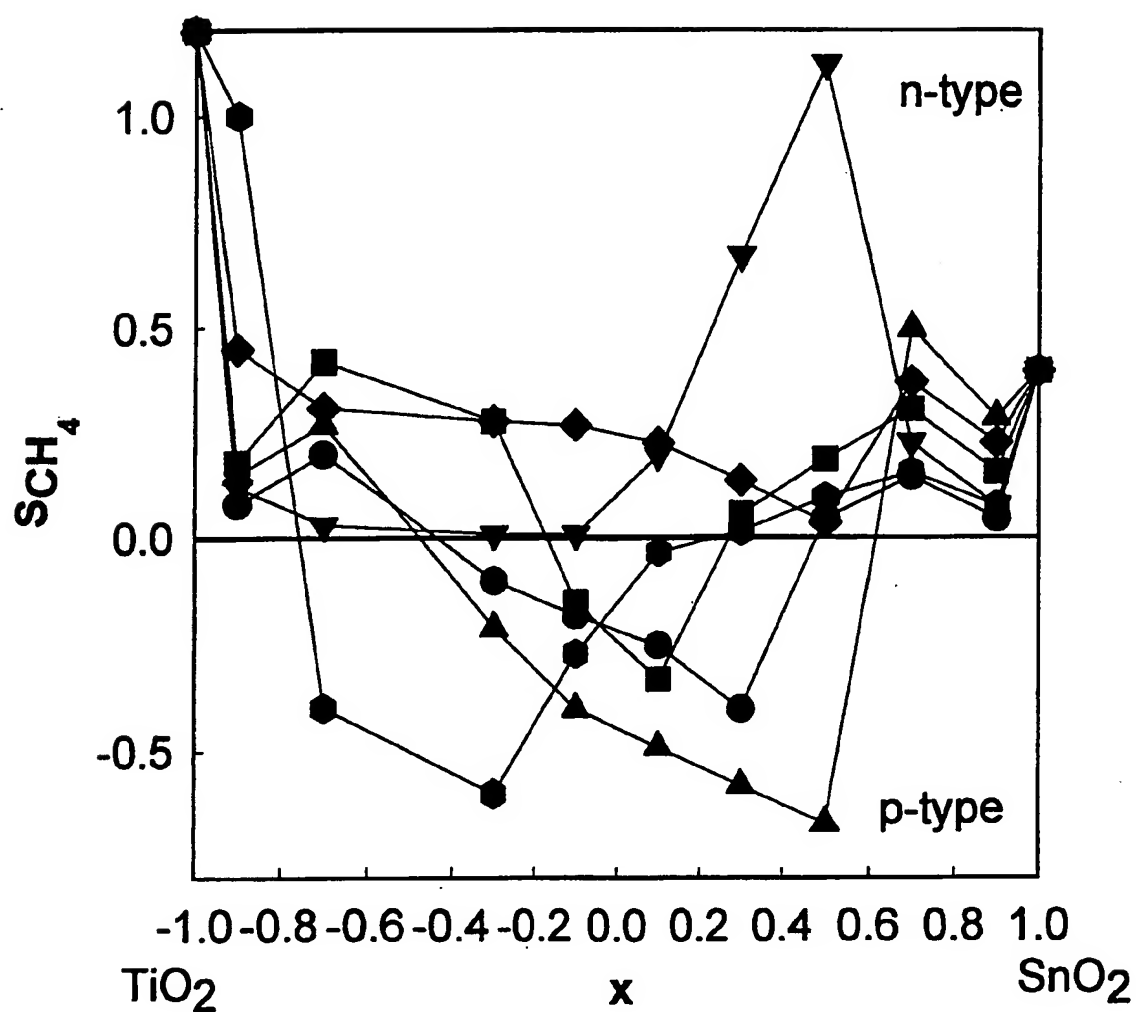
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FIG. 4



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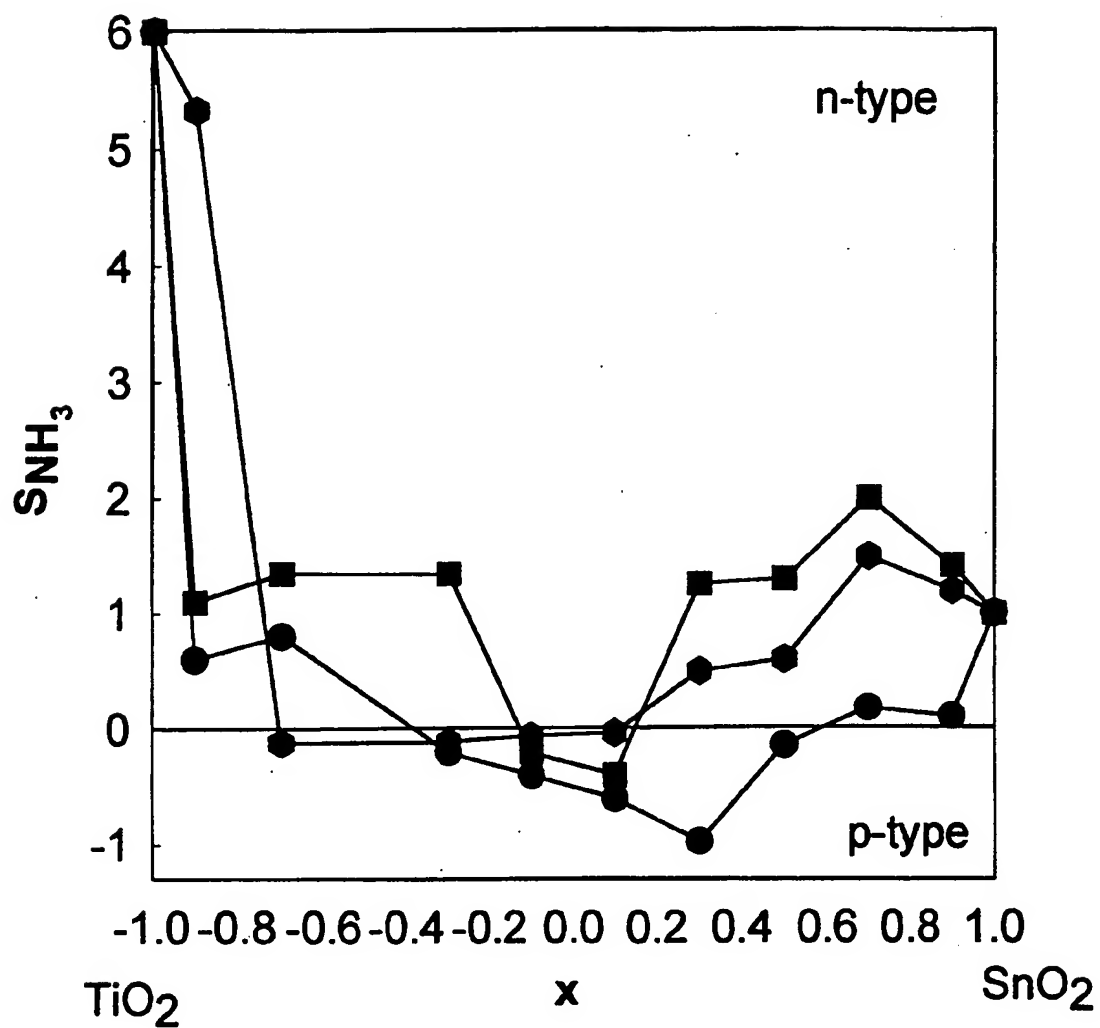
FIG. 5



- Mn [Ar]3d⁵4s²
- Fe [Ar]3d⁶4s²
- ▲ Co [Ar]3d⁷4s²
- ▼ Ni [Ar] 3d⁸4s²
- ◆ Cu [Ar] 3d¹⁰4s¹
- ⬢ Zn [Ar] 3d¹⁰4s²

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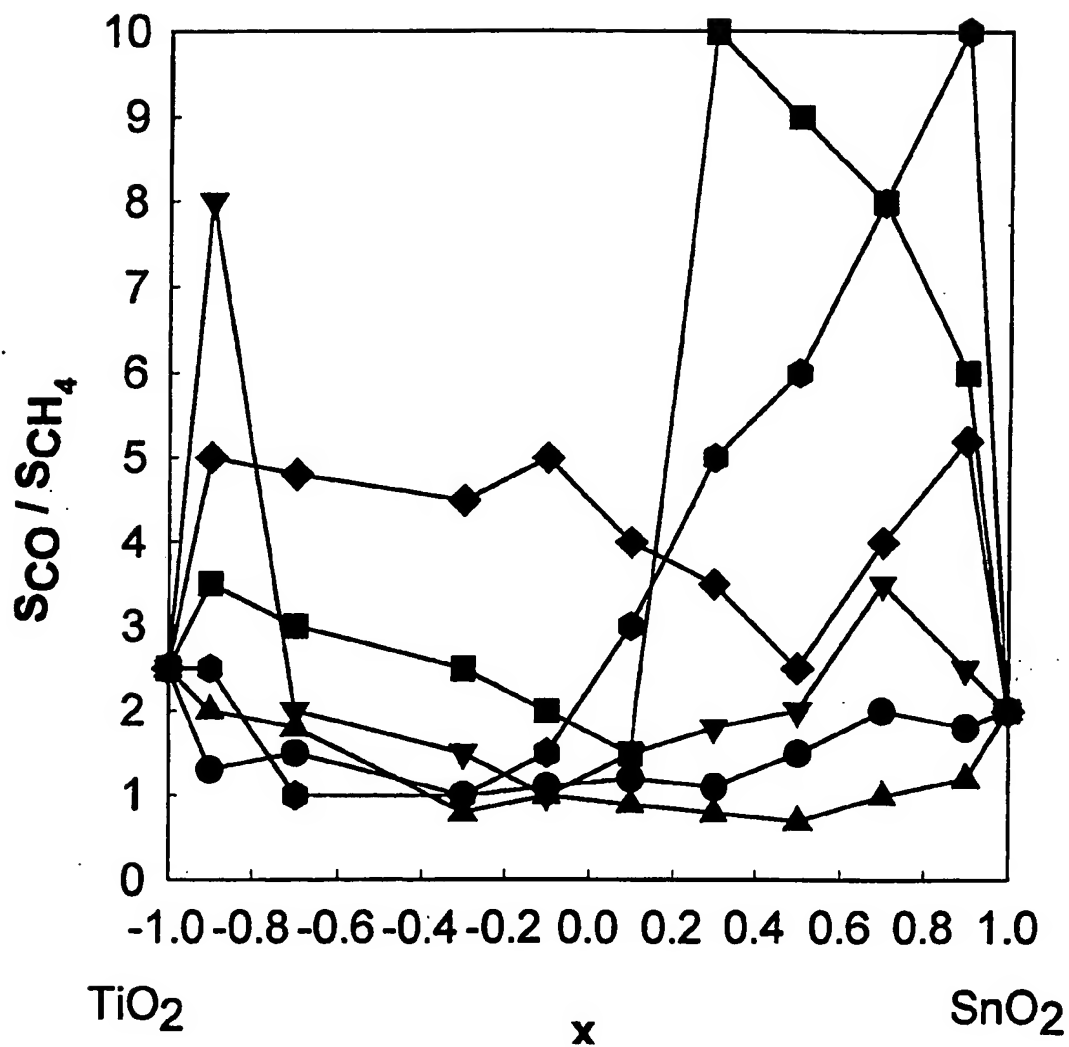
FIG. 6



- Mn $[Ar]3d^5 4s^2$
- Fe $[Ar]3d^6 4s^2$
- ◆ Zn $[Ar]3d^{10} 4s^2$

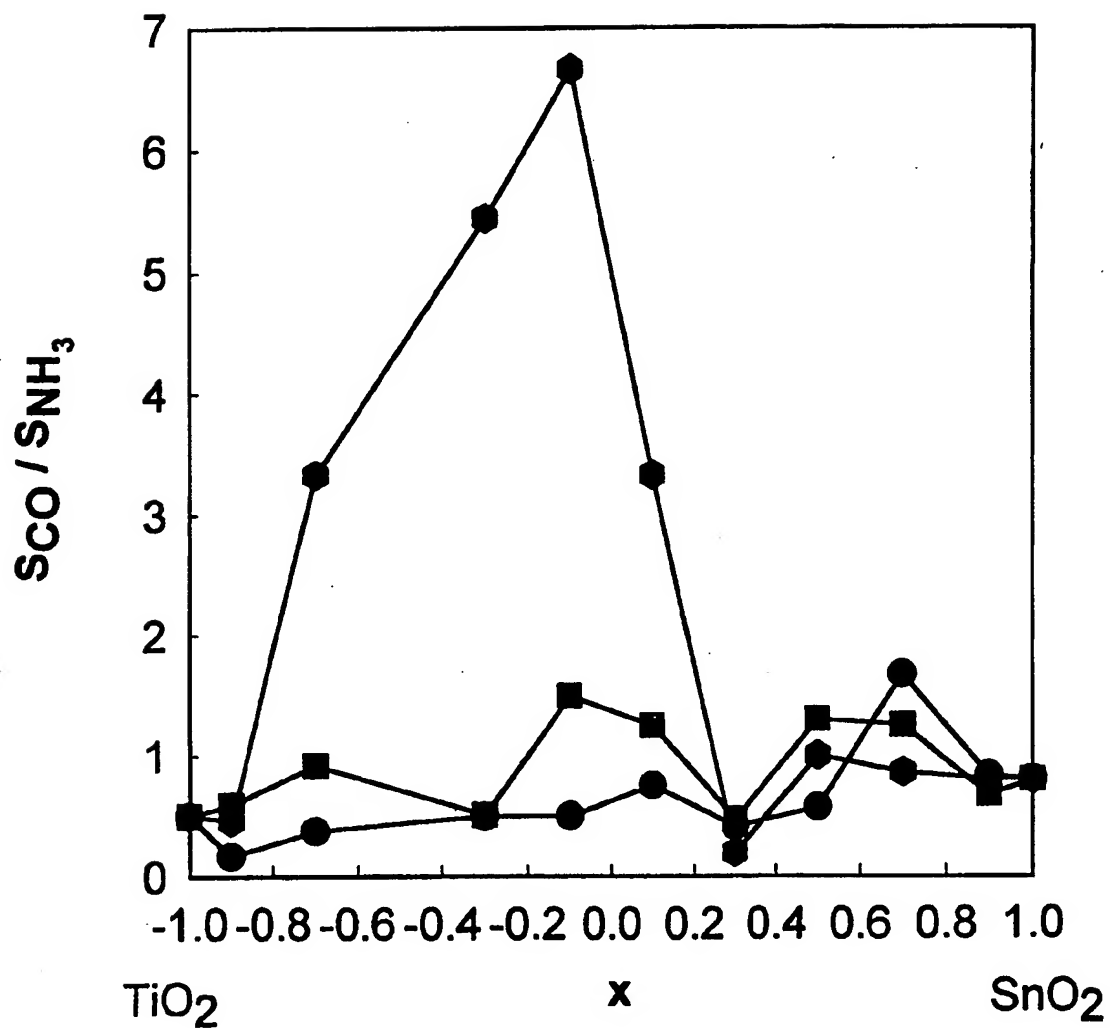
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FIG. 7



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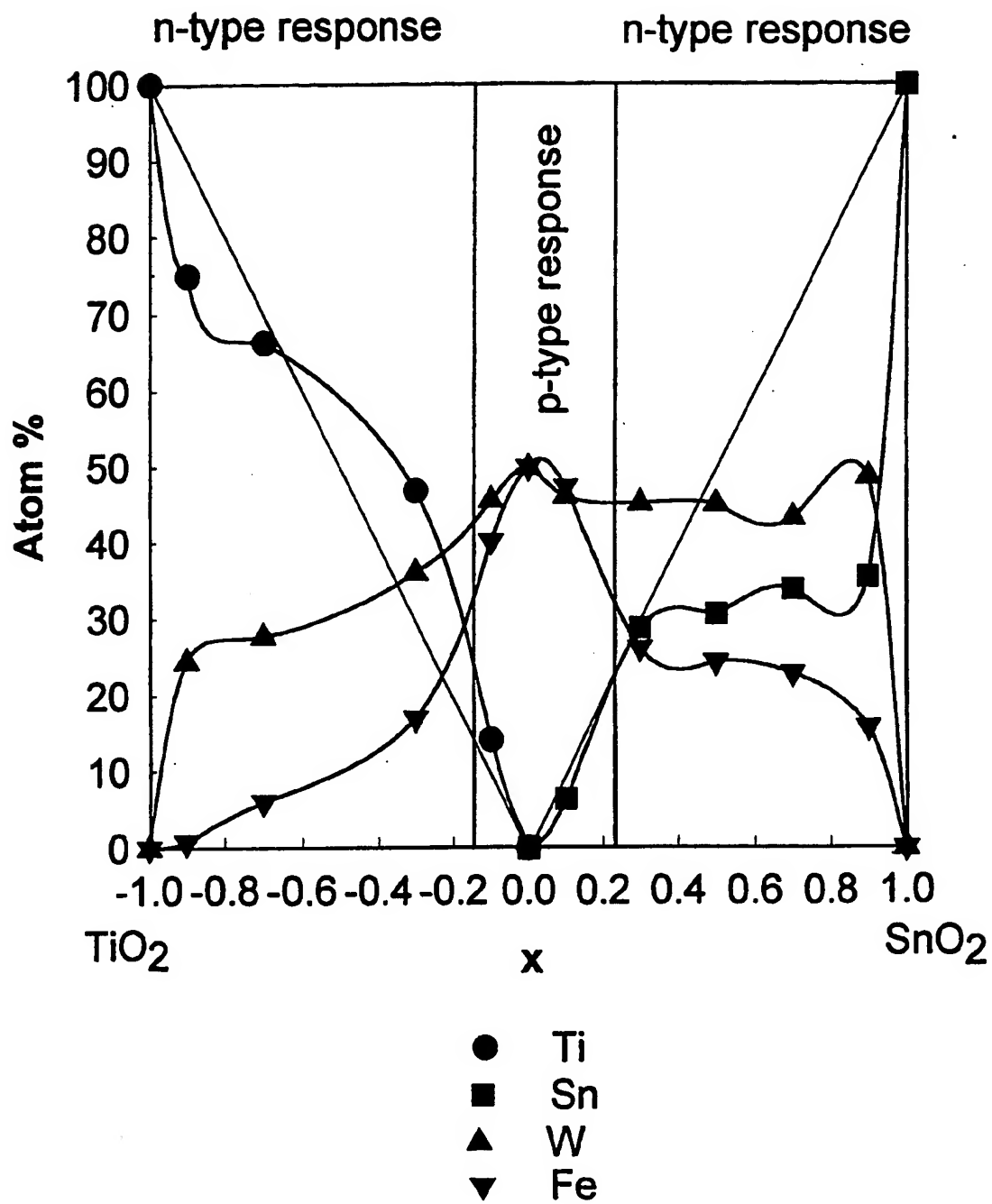
FIG. 8



- Mn [Ar]3d⁵4s²
- Fe [Ar]3d⁶4s²
- Zn [Ar] 3d¹⁰4s²

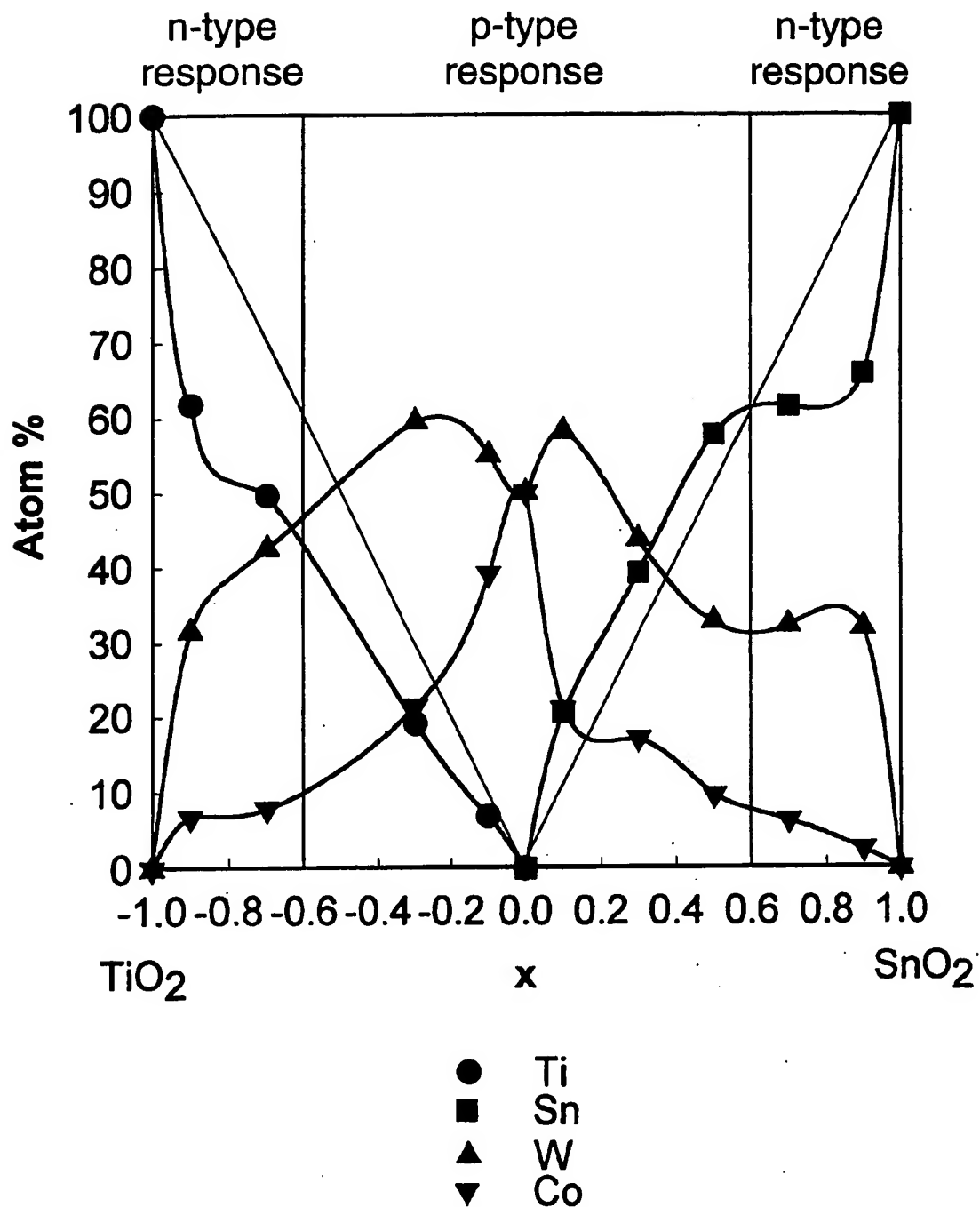
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FIG. 9



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FIG. 10



INTERNATIONAL SEARCH REPORT

Inter. Appl. No.
PCT/GB 99/03160

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
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